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Preparation of 1, 4-Butanediol Monovinyl Ether and its Polymerization

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ABSTRACTS

Preparation of 1,4-Butanediol Monovinyl Ether and its Polymerization

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1,4-Butanediol monovinyl ether is prepared by the vinylation of 1,4-butanediol in the presence of KOH. The vinyl ether is polymerized in bulk and in solution by Friedel-Crafts catalysts, and a viscous linear polyacetal $\text{CH}_2=\text{CH}-(\text{OC}_4\text{H}_8-\text{OCHMe})_n-\text{OC}_4\text{H}_8\text{OH}$ is formed.

The Vinylation of 1, 4-Butanediol.

A 1.2-l. autoclave is charged with a solution of 9g. of KOH in 180g. of $(\text{CH}_2\text{CH}_2\text{OH})_2$ and 170g. of tetrahydrofuran and then equimolecular C_2H_2 is compressed in. It is carefully heated with stirring to 140° and kept at $140\sim 50^\circ$ until the decline of pressure is not observed (It requires about 8 hrs.). After removing tetrahydrofuran, Et_2O and H_2O is added, and the ether extract is washed with H_2O and dried over K_2CO_3 . Its fractional distillation yields 23.2g. (8.2%) of 1, 4-butanediol divinyl ether (I), b.p.₁₈ $65\sim 67^\circ$, n_D^{20} 1.4397, d_4^{20} 0.9071, 121g. (52%) of 1,4-butanediol monovinyl ether (II), b.p.₈₁ $83\sim 85^\circ$, n_D^{20} 1.4432, d_4^{20} 0.9448, and 20.8g. (12%) of unreacted 1, 4-butanediol (III). When the molar ratio of C_2H_2 to $(\text{CH}_2\text{CH}_2\text{OH})_2$ is increased to 1.5, the yields of I and II are 24% and 53%, respectively. If the reaction is run without tetrahydrofuran, 62% of I is obtained as main product with 8.2% of II. In the last two cases, acetylene is added repeatedly.

The Polymerization of 1,4-Butanediol Monovinyl Ether.

Bulk Polymerization: To 10 g. of II is added dropwise with vigorous stirring 1.3 c.c. of 3% SnCl_4 in petroleum ether at $10\sim 15^\circ$. After keeping for 7 hrs. with stirring at that temperature, 5 c.c. of 10% K_2CO_3 solution and 20 c.c. of benzene are added to the reaction product to deactivate the catalyst. The benzene layer is separated, washed with H_2O , and the low boiling matter removed by heating to 80° at 5mm. Thus, a transparent, viscous polymer is obtained in 80% yield (8.0g). Intrinsic viscosity $[\eta]=0.13$ (20°C , benzene solution, concentration unit g/100ml). Average molecular weight 2,470 (cryoscopic method). II is similarly polymerized with SnCl_4 , AlCl_3 and $\text{BF}_3\cdot\text{Et}_2\text{O}$ at the same temperature. Of these catalysts, AlCl_3 gives the polymer of the highest average molecular weight (3,600). On the other hand, BF_3 gives only a low polymer at $25\sim 28^\circ$. With $\text{BF}_3\cdot\text{Et}_2\text{O}$, no polymerization is observed at $-35\sim -30^\circ$ during 3 hrs., but at $-25\sim -20^\circ$ a polymer is formed, and its average polymerization degree (29) is not different from that of the polymer formed at $10\sim 15^\circ$.

Solution Polymerization: Solution polymerization in a few solvents (CHCl_3 , $\text{C}_6\text{H}_5\text{CH}_3$ and Et_2O) at $15\sim 20^\circ$ with SnCl_4 , BF_3 and $\text{BF}_3\cdot\text{Et}_2\text{O}$ gives only a polymer of low polymerization degree in a low yield. The best results is obtained by polymerizing in CHCl_3 at $-40\sim -38^\circ$ with BF_3 . In this case the yield is 71%,

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and the average polymerization degree is 19.

The polymer is soluble in the most solvents, but insoluble in petroleum ether and water. It is easily decomposed by acid, and yields acetaldehyde. This fact points out that the polymer is a polyacetal.

Synthesis of an Anion-Exchange Resin from Methylvinylketone

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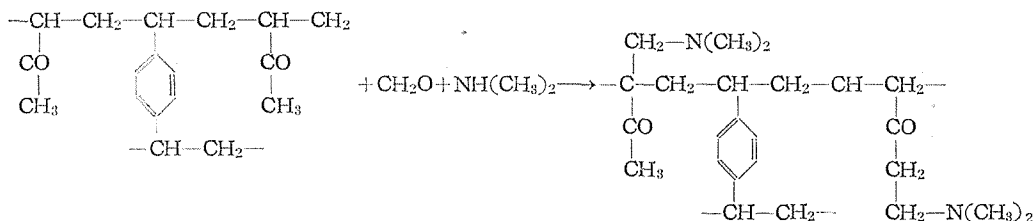
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Polymethylvinylketone has the active methylene and methyl groups adjacent to its carbonyl groups. Paying attention to these groups, the authors attempted the synthesis of an anion-exchange resin by the Mannich reaction on methylvinylketone-divinylbenzene copolymer.

The starting copolymer was prepared by the bulk polymerization of methyl vinyl ketone and divinylbenzene (molar ratio 95 : 5) using azobisisobutyronitrile as initiator. The above polymer was suspended in dioxane, formaldehyde and dimethylamine were added, and the mixture was refluxed for ca. 25 hrs. The structure of the obtained resin could be written as follows.



The nitrogen content of this resin was found as 8.24%, i.e., the degree of aminomethylation was 62%. The ionexchange capacity was measured by the usual method. It was 5.66 m. eq./g. of dried resin, while the theoretical value calculated from the nitrogen content was 5.88 m. eq./g.

In order to quarternize the amino group, the aminated resin was treated with dimethyl sulfate or methyl iodide in dioxane for ca. 12 hrs. at 40-50°C and then allowed to stand room temperature for 50 hrs. Only 23% of total amino groups was quarternized. The ability of decomposing neutral salt was 1.15 m. eq./g. The difficulty in quarternization may be due to the deamination and intra- or inter-molecular recombination.